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THE APPLICATION OF THE EXTENDED HUECKEL METHOD TO THE CALCULATION OF RATE RATIOS AND ACTIVATION ENERGIES.

THE ENOLIZATION OF SOME METHYL KETONES.

William H. Sachs and Christoffer Rappe

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

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Recent developments in quantum chemistry now permit a wide variety of M. O. calculations on organic compounds of theoretical and practical interest in which the σ- framework is explicitly included. Thus far, however, these calculations have been largely limited to the calculation of heats of atomization (1) and conformational energies (2). Hoffmann has also considered a number of carbonium ion intermediates (transition states), as has Wiberg (1b,2).

In this communication, we report the application of the extended Hückel method (2) to the calculation of thermodynamic stability differences (rate ratios) for the enolization of a number of structurally simple methyl ketones which have been studied experimentally (3). In the case of enols, activation energies are deduced from the energy difference of the respective enol and ketone.

Enols and enolates derived from methyl ketones are ideal for such calculations because the number and types of atoms are the same for the 1- and 3-enols and enolates, respectively. The energy differences calculated for the 1- and 3-enols (enolates) will therefore reflect differences in their stabilities and hence rates of formation. In order for these energy differences to be meaningfully related to experimental rate ratios for acid- and base-catalyzed enolization (deuteration), a detailed knowledge of the transition state for enolization is required, and ideally, calculations should be carried out on these structures. In the absence of such knowledge, we have carried out calculations on the enols (for an enol-like transition state) for acid-catalyzed enolization, and on the enolates (for an enolate-like transition state) for base-catalyzed enolization. The latter approximation may be in error as there are cases in the literature where the transition state for base-catalyzed enolization has been infered as ketone-like (3b,4). However, the degree to which experiment and calculation agree should be some measure of the validity of the approximations introduced. One additional approximation, and perhaps the most serious one, deserves mention. This is the isolated-molecule approximation (5) in which specific solvation effects, entropy, and zero-point vibrational energy differences are conspicuously neglected. Of these, the neglect of solvent-substrate interactions is probably the most serious, and indeed, there is evidence that the nature of the solvent can affect the orientation of enolization (3,6).

Calculations were carried out on only one conformation for each enol, enolate, and ketone studied. Calculations were not made on larger ketones and enols because of the increased number of rotational degrees of freedom and the inherent difficulty in intuitively choosing the low energy conformation. Conformations were chosen which reflect as much as possible what is known about conformational minima in similar systems (7). Table I lists the bond lengths and angles used in calculating the atomic coordinates, as well as the other input parameters. The results of the calculations and the experimental values are listed in Table II.

Table I.

Bond lengths (internuclear distance)		Bond angles		Ionization potentials(8)		Slater coefficients
C-C	1.54Å	sp^3 carbon	109.5°	carbon(2s)	-21.4eV	1.625
C=C	1.33	sp^2 carbon	120.0°	carbon(2p)	-11.4	1.625
C-H	1.09	H-C-H (cyclopropane)	114.0°	hydrogen(1s)	-13.6	1.000
C=O	1.21			oxygen(2s)	-35.0	2.275
C-O	1.21	C-C-C (cyclopropane)	60.0°	oxygen(2p)	-17.5	2.275
O-H	0.96	C-O-H	109°			
C-C (cyclopropane)	1.51					

Table II.

Ketone $R-CO-CH_3$ R	Base-catalysis Hückel[a] ΔE(kcal)	Base-catalysis Exptl[a] ΔE	Acid-catalysis Hückel ΔE	Acid-catalysis Exptl ΔE	Activation Energy[b] Hückel ΔE*	Activation Energy[b] Exptl ΔE*
CH_3CH_2	0.2[d]	0.36[e]	-1.4[d]	-0.40[e]	45.1	-
$CH_3CH_2CH_2$	-6.9	0.75[e]	-6.9	-0.29[e]	52.3	-
$(CH_3)_2CH$	13.5	2.86[e]	14.1	0.14[e]	60.1	25.9 ± 3. 26.4 ± 2.
$(CH_2)_2CH$	-	>3.0	-	>3.0	68.0	27.0 ± 2.
$(CH_2)_2CHCH_2$	-6.1	-	-5.5[e]	-0.46[e]	-	-

a) ΔE(Hückel) = E(3-enol(ate)) - E(1-enol(ate)). ΔE(Exptl) = RT·ΔA = RT·ln(k_{CH_n}/k_{CH_3}). Values are calculated for 313°K and ΔA is assumed to be zero. The ΔE's are given in kcal/mole. b) The activation energies(Hückel) are given for the formation of the 1-enol. The values for the 3-enols are obtained by adding the appropriate ΔE. c) These energies have been calculated from data in ref 3d. d) Ref 3a. e) Ref 9.

It is seen that in all but one case (the enolates of 2-pentanone), the _orientation_ of enolization is correctly calculated, but that the absolute energy differences are much too large and that there is no qualitative ordering in the values. Agreement is lacking between calculated and _preliminarily_ determined activation energies, however, the ketones are in all cases calculated to be more stable than the enols by a large factor, in agreement with observation.

Refined SCF calculations of the type recently described by Pople, _et al_ (10), by Dewar, _et al_ (1a), and by Wiberg (1b) might give better results, but they will still be subject to the same approximations set forth in the beginning of this paper. Perhaps better results are to be obtained for calculations on reactions in the gas-phase where solvent-substrate interactions are at a minimum.

It must be concluded that the desired accuracy in the calculation of kinetic effects by the Hückel method is wanting. As a tribute to the method, it is surprising that the measure of success in this investigation is as great as it is.

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